

Aerobic aquatic metabolism of Transfluthrin in two test systems

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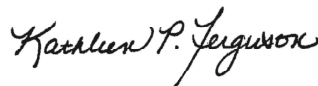
Statements: The study was conducted according to USEPA, OECD, and German GLP standards (p. 3). Signed and dated Data Confidentiality, GLP, and Quality Assurance statements were provided (pp. 2-3, 60). A certification of the authenticity of the study was provided in the Quality Assurance statement (p. 60).

Classification: This study is classified as **Supplemental**. The first sample was not collected until 1 day posttreatment, at which time transfluthrin was only 73.23-74.30% of the applied. Sampling intervals were widely spaced, so that in some cases the concentrations of transformation products changed abruptly between intervals. Material balances were variable in both test systems and <90% of the applied at 100 days in the Laacherhof water:silt loam sediment systems Pesticide use history at the collection sites was not reported, and it was not confirmed that the sediments were free of pesticides prior to use. Limits of Detection and Quantification were not reported.

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Final EPA Reviewer: He Zhong, Ph.D. Signature: Date: 6/7/2017
Biologist

CDM/CSS-Dynamac JV Reviewers: Mary Samuel, Signature:  Date: 5/16/17
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This Data Evaluation Record may have been altered by the Environmental Fate and Effects Division subsequent to signing by CDM/CSS-Dynamac JV personnel.

Executive Summary

The aerobic transformation of [2,3,5,6-tetrafluorophenyl- ^{14}C -methylene]transfluthrin (benflurthrin; NAK 4455) was studied in two water:silt loam sediment systems (Laacherhof: water pH 8.6, sediment pH 6.5 and organic carbon 5.0%; and Hönniger Weiher: water pH 7.6, sediment pH 5.4 and organic carbon 3.7%) from Germany in closed systems treated at 41.8 μg a.i./sample (83.6 $\mu\text{g/L}$) and incubated in the dark at 20°C for up to 100 days. Duplicate samples (two entire flasks) of each test system were collected at 1, 7, 28, and 100 days. A single sample (one entire flask) of each

test system was collected at 70 days. In the water column of the Laacherhof water:silt loam sediment systems following treatment, measured redox potentials, oxygen saturation and pH were +119 to +322 mV, 43-82% and 4.8-8.5, respectively, with measured redox potentials in the sediment of -69 to +70 mV. In the water column of the Hönniger Weiher water:silt loam sediment systems following treatment, measured redox potentials, oxygen saturation and pH were +174 to +270 mV, 45-95% and 5.5-8.3, respectively, with measured redox potentials in the sediment of -117 to -29 mV. The water of both systems was oxic and the sediment generally suboxic throughout the experiments. The two test systems were viable at study termination.

In the Laacherhof water:silt loam sediment systems, recoveries averaged $94.3 \pm 8.3\%$ (sample range 81.53-106.40%) of the applied. Recoveries were within guideline criteria (90% - 110%) except at 100 days. In the water column, transfluthrin decreased from a maximum of 23.5% of the applied at 1 day posttreatment to 1.2% at 7 days and was not detected at and after 28 days. In the sediment, transfluthrin was a maximum of 54.0% at 1 day and decreased to 3.3% at 100 days.

In the Hönniger Weiher water:silt loam sediment, recoveries averaged $95.0 \pm 7.3\%$ (sample range 80.92-106.62%) of the applied. Recoveries were within guideline criteria (90% - 110%) except for a single replicate at 7 days. In the water column, transfluthrin was detected at a maximum of 39.1% of the applied at 1 day posttreatment to 3.7% at 7 days and was not detected at and after 28 days. In the sediment, transfluthrin was a maximum of 64.4% at 1 day and decreased to 3.1% at 100 days.

Observed DT₅₀ values, calculated half-lives, and information on transformation products are listed in **Table 1**. Transfluthrin dissipated with a SFO DT₅₀ values of 13.5 days in the Laacherhof water:silt loam sediment systems and 5.93 days in the Hönniger Weiher water:silt loam sediment systems. Product profiles were comparable between the two systems. Two transformation products were identified.

In the water from the Laacherhof water:silt loam sediment systems, radioactive residues were 40.41% of the applied at 1 day posttreatment, a maximum of 59.36% at 70 days, and 51.89% at 100 days. In the sediment, extractable radioactivity was 48.99% at 1 day, a maximum of 67.58% at 7 days, and 22.18% at 100 days. Unextracted radioactivity was a maximum of 8.56% at 1 day and decreased to 4.55% at 100 days. CO₂ and volatile organic compounds totaled maximums of 3.07% and 2.86%, respectively, at 100 days.

In the water from the Hönniger Weiher water:silt loam sediment systems, radioactive residues were 48.08% of the applied at 1 day posttreatment, a maximum of 63.80% at 7 days, and 53.60% at 100 days. In the sediment, extractable radioactivity decreased from a maximum of 59.93% at 1 day to 25.11% at 100 days. Unextracted radioactivity was a maximum of 8.56% at 1 day and was 7.95% at 100 days. CO₂ totaled a maximum of 13.35% of the applied at 100 days posttreatment. Volatile organic compounds were a maximum 1.52% at 7 days and were 0.33% at 100 days.

Table 1. Results Synopsis: Aerobic Aquatic Metabolism of Transfluthrin in the Total System¹

Total System	Observed DT ₅₀ (days)	Calculated Half-life (days) ¹	Model Parameters and Statistics ¹	Transformation Products Common Name (maximum % AR, associated interval) ²	
				Major	Minor
Germany Laacherhof Water:silt loam sediment (20°C, water pH 8.7, sediment pH 6.5)	7-28	13.5 SFO	C ₀ = 76.7 k = 0.0512 S _C = 114 S _{SFO} = 113	NAK 4723 (80.63%, 70 days)	NAK 4452 (6.43%, 1 day) CO ₂ (3.07%, 100 days)
Germany Hönniger Weiher Water:silt loam sediment (20°C, water pH 7.6, sediment pH 5.4)	1-7	5.93 SFO	C ₀ = 73.8 k = 0.117 S _C = 689 S _{SFO} = 633	NAK 4452 (52.86%, 7 days) NAK 4723 (83.35%, 28 days) CO ₂ (13.35%, 100 days)	None

¹ Calculated half-lives, model parameters, and kinetics models in accordance with the NAFTA kinetics guidance (USEPA, 2012); Single First-Order (SFO).

² AR means “applied radioactivity”.

I. Materials And Methods

A. Materials:

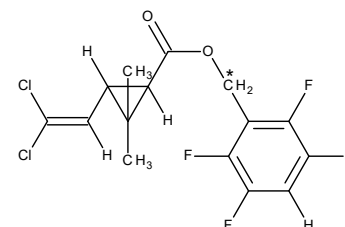
1. Test Material [2,3,5,6-Tetrafluorophenyl-¹⁴C-methylene]transfluthrin (benfluthrin; NAK 4455; pp. 8, 12; Appendix 4, p. 31)

Specific activity: 3.90 MBq/mg, 105 µCi/mg (p. 12)

Radiochemical purity: ≥98.7%

Chemical purity: Not reported

Sample ID: Not reported



Solubility in water (20°C) 57 µg/L at pH 5-7 (Appendix 4, p. 31)

2. Reference Compounds: The following compounds were used in the analysis.

Table 2. Reference Compounds

Applicant's Code Name	Chemical Name	Purity (%)	Batch ID
Transfluthrin (Benfluthrin, NAK 4455)	(2,3,5,6, Tetrafluorophenyl) methyl ester 3-(2,2-dichloroethenyl)-2,2-dimethyl-cyclopropane carboxylic acid	98.0	--
NAK 4723	2,3,5,6-Tetrafluorobenzoic acid	--	
NAK 4452	2,3,5,6-Tetrafluorobenzyl alcohol	--	--

Data obtained from p. 12 and Appendices 4-5, pp. 31-32, of the study report.

-- No information.

3. Water:Sediment: Water and sediment collection and characterization are summarized in **Table 3** and **Tables 4a-4b**, respectively.

Table 3. Water:Sediment Collection and Storage.

Description		Laacherhof	Hönniger Weiher
Geographic location		Monheim, Germany	Close to Wipperfürth, North Rhine-Westphalia, Germany
Site description		Natural pond (ca. 500 m ² surface area) with no inflow or outflow; oligotrophic	Artificially dammed pond (1,000 m ² surface area) in the course of Hönniger Bach River, and has a strong water current, mesotrophic/eutrophic
Pesticide use history at the collection site		Not reported	
Collection date		September 1, 1992	September 4, 1992
Collection procedures	Water:	Not reported	
	Sediment:	Collected from center of pond; top ca. 2-4 cm scraped off with flat scoop and put in containers	Collected 2 m from steep bank; top ca. 2-4 cm scraped off with flat scoop and put in containers
Storage conditions	Water:	At room temperature	
	Sediment:		

Description		Laacherhof	Hönniger Weiher
Storage length		ca. 3 weeks, based on a study start date of September 24, 1992	
Preparation	Water:	Sieved (2-mm mesh)	
	Sediment:		

Data obtained from pp. 11, 14, in the study report.

Table 4a. Parameters for Characterization of Water:Sediment Samples – Laacherhof

Parameter (unit)		Field Sampling/Post Handling	Stage of Test Procedure		
			Day 0	Day 28	Day 100
Water					
Temperature (°C)		--			
pH ¹		8.6, 8.7	8.2	7.9	4.8, 5.1
Hardness (°DH)		--			
TOC (mg/L)		--	--		--
O ₂ Content (%)		--	82	68, 69	79, 85
Measured redox potential (mV)			+178	+187, +201	+292, +322
Sediment					
Sampling Depth		ca. 2-4 cm			
pH	In water	6.6	-- ¹	--	--
	In CaCl ₂	6.5			
Soil Texture (USDA)		Silt loam			
Particle Size Distribution (%)	Sand (2000 - 63 μm)	29.9			
	Silt (63 – 2.0 μm)	64.7			
	Clay (<2 μm)	5.4			
Organic matter (%) ²		8.6			
Organic carbon (%)		5.0			
CEC (meq/100 g)		--			
Microbial biomass (mg CO ₂ /hr/kg sediment)		--	--		9
Measured redox potential (mV)			+1	+59, +70	-4, +51

Data obtained from p. 10; Appendix 3, p. 30; Appendix 6, p. 33 (for pH of the water posthandling); and Appendix 9, p. 36, in the study report. Sediment textures were reported using the DIN system. USDA sediment textures were approximated by the reviewer using USDA-NRCS technical support tools.

1 The pH reported for the water is from the start of preincubation (Appendix 6, p. 33). Except for the post-handling sediment in CaCl₂ and water, pH was reported only for the total test system. It was not specified if the pH was measured in the water, sediment, or water:sediment interface.

2 Calculated by the reviewer as organic matter (%) = organic carbon (%) x 1.72.

-- = not reported

Table 4b. Parameters for Characterization of Water:Sediment Samples – Hönniger Weiher.

Parameter (unit)	Field Sampling/Post Handling	Stage of Test Procedure		
		Day 0	Day 28	Day 100
Water				
Temperature (°C)	--			
pH ¹	7.6	7.8	6.1, 6.3	7.0, 7.4
Hardness (°DH)	4.2			
TOC (mg/L)	2	--		--
O ₂ Content (%)	--	83	60, 66	94, 95
Measured redox potential (mV)		+225	+240, +270	+230, +247

Parameter (unit)		Field Sampling/Post Handling	Stage of Test Procedure		
			Day 0	Day 28	Day 100
Sediment					
Sampling Depth		ca. 2-4 cm			
pH	In water	5.8	-- ¹	--	--
	In CaCl ₂	5.4			
Soil Texture (USDA)		Silt loam			
Particle Size Distribution (%)	Sand (2000 - 63 μm)	24.4			
	Silt (63 – 2.0 μm)	72.0			
	Clay (<2 μm)	3.6			
Organic matter (%) ²		6.4			
Organic carbon (%)		3.7			
CEC (meq/100 g)		--			
Microbial biomass (mg CO ₂ /hr/kg sediment)		--	--		13
Measured redox potential (mV)			-117	-50, -40	-44, -29

Data obtained from p. 10; Appendix 3, p. 30; Appendix 6, p. 33 (for pH of the water posthandling); and Appendix 9, p. 36, in the study report. Sediment textures were reported using the DIN system. USDA sediment textures were approximated by the reviewer using USDA-NRCS technical support tools.

1 The pH and O₂ content reported for the water is from the start of preincubation (Appendix 6, p. 33). Except for the post-handling sediment in CaCl₂ and water, pH was reported only for the total test system. It was not specified if the pH was measured in the water, sediment, or water:sediment interface.

2 Calculated by the reviewer as organic matter (%) = organic carbon (%) x 1.72.

-- = not reported

B. Study Design

1. **Experimental Conditions:** Table 5 summarizes the experimental conditions.

Table 5. Experimental Design.

Experimental Design	Laacherhof	Hönniger Weiher
Duration of the test	100 days	
Water:		
Type and size of filter used	2-mm mesh	
Amount of sediment and water per treatment:		
Water (mL)	500	490
Sediment (g)	195	205
Water:sediment ratio	ca. 2:1, v:v, based on an ca. 2 cm depth of sediment covered with ca. 4.5 cm layer of water	
Application rates:		
Nominal	40 µg/sample	
Actual	41.8 µg/sample	
Number of replicates:		
Control, if used	Sterile controls were not used.	
Treated	Duplicate samples (two entire flasks) of each test system were collected at 1, 7, 28, and 100 days. A single sample (one entire flask) of each test system was collected at 70 days.	
Test apparatus:		

Experimental Design	Laacherhof		Hönniger Weiher	
Type/material/volume	The test system consisted of glass vessels (1 L volume, i.d. <i>ca.</i> 10 cm) containing water and sediment that were acclimated for <i>ca.</i> 11 days prior to treatment. Following treatment, the flasks were sealed with glass tubes containing a polyurethane foam plug (nearest the soil) and alternating layers of cotton wool and soda lime. The tubes were open to the atmosphere. The water layer was continually agitated with a magnetic stirrer (60 rpm). Samples were incubated in the dark under temperature-controlled conditions. The test system is illustrated in Appendix 1, p. 28.			
Details of traps for CO ₂ and organic volatile, if any	Volatiles were trapped passively using a polyurethane foam plug and soda lime. Prior to opening a vessel, the headspace gases were purged with air through the volatile trap for <i>ca.</i> 10 minutes. A subsample of the water was analyzed for dissolved CO ₂ . The volatile trapping system is illustrated in Appendix 1, p. 28, and Appendix 7, p. 34.			
If no traps were used, is the system closed?	Volatile traps were used.			
Identity and final concentration (based on water volume) of co-solvent	Ethanol, <0.05% by volume			
Test material application method:				
Volume of the test solution used/treatment	190 µL/sample			
Application method (<i>i.e.</i> , mixed/not mixed)	Applied to the water surface using a pipette. The water was continually agitated during the study.			
Any indication of the test material adsorbing to the walls of the test apparatus?	None			
Microbial biomass in untreated samples (mg CO ₂ /hr/kg sediment)	Initial	Final	Initial	Final
Water	Not reported			
Sediment	--	9	--	13
Experimental conditions:				
Temperature	20 ± 2°C, range not reported			
Continuous darkness (yes/no)	Yes			
Other details (if any)	None			

Data obtained from pp. 13-16; Appendix 1, p. 28; Appendix 3, p. 30; and Appendices 7-8, pp. 34-35, of the study report.

2. Sampling during Study Period: Table 6 summarizes sampling during the study period.

Table 6. Sampling during Study Period.

Parameter	Details
Sampling intervals	1, 7, 28, 70, and 100 days posttreatment.
Sampling method	Duplicate samples (two entire flasks) of each test system were collected at 1, 7, 28, and 100 days. A single sample (one entire flask) of each test system was collected at 70 days.
Method of collection of CO ₂ and organic volatile compounds	Volatile traps were collected at each sampling interval. Water subsamples were analyzed for dissolved CO ₂ at each sampling interval.
Sampling Intervals/Times	
Redox potential in water layer	Measured at time 0 and each sampling interval
Dissolved oxygen in water layer	
pH in water layer	
Redox potential in sediment	
pH in sediment	

Parameter	Details
Other details, if any	Length and conditions of storage of the samples prior to analysis was not reported.

Data obtained from pp. 15 and Appendix 9, p. 36, of the study report.

3. Analytical Procedures:

Separation of the Water and Sediment: The water layer was decanted from the sediment, then centrifuged and filtered (pp. 15-16). Aliquots of the water and filter paper were analyzed using LSC. An aliquot of the water was reacted with HCl for *ca.* 1 hour with stirring; released volatiles were trapped and analyzed using LSC.

Extraction/Clean Up/Concentration Methods: At 1, 7 and 28 days, the water was partitioned twice with dichloromethane (p. 16). The water fraction from 7 days was further extracted with dichloromethane at pH 3 or 8 (p. 16; Appendix 11, p. 38). Aliquots of the dichloromethane and water fractions were analyzed using LSC. Aliquots of the dichloromethane fractions were analyzed by TLC. The water fractions were freeze-dried and the resulting residues dissolved in methanol and analyzed by LSC and TLC.

At 70 and 100 days, the water was freeze-dried after filtration, and the resulting residues dissolved in methanol and analyzed by LSC and TLC (p. 16).

The sediments were transferred into centrifuge beakers that had held the water (so that solids in the water were combined with the sediment) and extracted three times with acetonitrile by shaking (overnight, then for 2 hours, then a rinse) at room temperature (p. 17). After each extraction, the samples were centrifuged and the supernatant filtered. The extracts were combined, and aliquots were analyzed using LSC and TLC. The filter paper was analyzed using LSC following combustion.

Determination of Unextracted Residues: Portions of the extracted soils were air-dried, ground and analyzed for total remaining radioactivity using LSC following combustion (p. 18).

Determination of Volatile Compounds: The polyurethane foam plugs were extracted with acetonitrile by ultrasound, and aliquots of the extracts were analyzed using LSC and TLC (p. 17). The soda lime was reacted with HCl, and escaping gases were trapped in carbosorb/permafluor cocktail) and quantified using LSC (p. 17; Appendix 13, p. 40). Residues in the trapping solutions were not confirmed to be CO₂.

Total radioactivity measurement: Total [¹⁴C]residues were determined by summing the concentrations of residues in the water, sediment extracts, extracted sediment, and volatile traps (Appendix 14, p. 41).

Derivatization method: A derivatization method was not employed.

Identification and quantification of Parent and Transformation Compounds: Aliquots of the concentrated extracts were analyzed by two-dimensional TLC on silica gel plates developed in toluene:methanol (9:1, v:v) and toluene:hexane (2:1, v:v; pp. 18-19). Radioactive regions of interest were identified by comparison to the mobility of reference standards.

Detection Limits (LOD, LOQ) for the Parent and Transformation Products: Limits of Detection (LOD) and Quantification (LOQ) were not reported.

II. Results and Discussion

A. Data:

Study results, including total mass balances and distribution of radioactivity, are presented in **Tables 7a-7b**.

In the water column of the Laacherhof water:silt loam sediment systems following treatment, measured redox potentials, oxygen saturation and pH were +119 to +322 mV, 43-82% and 4.8-8.5, respectively, with measured redox potentials in the sediment of -69 to +70 (Appendix 9, p. 36). In the water column of the Hönniger Weiher water:silt loam sediment systems following treatment, measured redox potentials, oxygen saturation and pH were +174 to +270 mV, 45-95% and 5.5-8.3, respectively, with measured redox potentials in the sediment of -117 to -29 mV. The water of both systems was oxic and the sediment generally suboxic throughout the experiments.

The two test systems were viable at study termination (Appendix 3, p. 30).

B. Mass Balance:

In the Laacherhof water:silt loam sediment systems, recoveries averaged $94.3 \pm 8.3\%$ (sample range 81.53-106.40%) of the applied (Appendix 14, p. 41). Recoveries were within guideline criteria (90% - 110%) except at 100 days. In the water column, transfluthrin decreased from a maximum of 23.5% of the applied at 1 day posttreatment to 1.2% at 7 days and was not detected at and after 28 days (calculated from Appendix 14, p. 41, and Appendix 18, p. 45). In the sediment, transfluthrin was a maximum of 54.0% at 1 day and decreased to 3.3% at 100 days (calculated from Appendix 14, p. 41, and Appendix 20, p. 47).

In the Hönniger Weiher water:silt loam sediment systems, recoveries averaged $95.0 \pm 7.3\%$ (sample range 80.92-106.62%) of the applied (Appendix 14, p. 41). Recoveries were within guideline criteria (90% - 110%) except for a single replicate at 7 days. In the water column, transfluthrin was detected at a maximum of 39.1% of the applied at 1 day posttreatment to 3.7% at 7 days and was not detected at and after 28 days (calculated from Appendix 14, p. 41, and Appendix 18, p. 45). In the sediment, transfluthrin was a maximum of 64.4% at 1 day and decreased to 3.1% at 100 days (calculated from Appendix 14, p. 41, and Appendix 20, p. 47).

C. Bound and Extractable Residues:

In the water from the Laacherhof water:silt loam sediment systems, radioactive residues were 40.41% of the applied at 1 day posttreatment, a maximum of 59.36% at 70 days, and 51.89% at 100 days (Appendix 14, p. 41). In the sediment, extractable radioactivity was 48.99% at 1 day, a maximum of 67.58% at 7 days, and 22.18% at 100 days (calculated). Unextracted radioactivity was a maximum of 8.56% at 1 day and decreased to 4.55% at 100 days (Appendix 14, p. 41).

In the water from the Hönniger Weiher water:silt loam sediment systems, radioactive residues were 48.08% of the applied at 1 day posttreatment, a maximum of 63.80% at 7 days, and 53.60% at 100 days (Appendix 14, p. 41). In the sediment, extractable radioactivity decreased from a maximum of 59.93% at 1 day to 25.11% at 100 days (calculated). Unextracted radioactivity was a maximum of 8.56% at 1 day and was 7.95% at 100 days (Appendix 14, p. 41).

D. Volatilization:

In the Laacherhof water:silt loam sediment systems, CO₂ totaled a maximum of 3.07% of the applied at 100 days posttreatment (Appendix 21, p. 48). Volatile organic compounds were a maximum 2.86% at 100 days (calculated from Appendix 17, p. 44).

In the Hönniger Weiher water:silt loam sediment systems, CO₂ totaled a maximum of 13.35% of the applied at 100 days posttreatment (Appendix 21, p. 48). Volatile organic compounds were a maximum 1.52% at 7 days and were 0.33% at 100 days (calculated from Appendix 17, p. 44).

Dissolved CO₂ (soluble carbonate) totaled up to 0.79% of the residues in the water (p. 23)

Table 7a. Aerobic transformation of Transfluthrin, expressed as a percentage of the applied radioactivity, in Laacherhof water:silt loam sediment maintained in the dark.

Sampling Interval (days)	1		7		28		70	100	
Replicate	A	B	A	B	A	B	A	A	B
Transfluthrin (NAK 4455)	74.30	71.16	50.68	57.45	17.85	15.27	8.88	3.99	4.55
NAK 4452	6.43	3.06	2.31	2.61	n.d.	n.d.	n.d.	n.d.	n.d.
NAK 4723	1.57	1.17	31.84	34.42	72.87	79.39	80.63	70.47	66.91
Remainder	3.92	5.84	4.44	4.75	1.69	0.30	1.98	0.74	2.69
Water	37.09	40.41	30.29	31.27	50.69	56.02	59.36	51.89	50.98
Total sediment	56.59	49.23	64.72	74.71	46.24	42.14	36.42	26.73	24.98
Extracted residues	48.99	40.67	58.18	67.58	40.66	37.10	30.97	22.18	20.66
Unextracted residues	7.60	8.56	6.54	7.13	5.58	5.04	5.45	4.55	4.32
Total volatiles	0.19	0.17	0.82	0.42	1.69	2.72	3.22	4.02	5.56
CO ₂	0.04	0.02	0.04	0.04	0.64	0.88	2.05	2.89	3.07
Volatile organics	0.18	0.17	0.80	0.40	1.20	2.14	1.24	1.34	2.86
Mass balance	93.87	89.81	95.83	106.40	98.62	100.88	99.00	82.63	81.53

Data obtained from Appendix 14, p. 41, and Appendix 21, p. 48, of the study report.

Concentration in extracted sediment calculated as total sediment minus unextracted residues. Residues in the PU plugs calculated from Appendix 17, p. 44.

n.d. = not detected.

Table 7b. Aerobic transformation of Transfluthrin, expressed as a percentage of the applied radioactivity, in Hönniger Weiher water:silt loam sediment maintained in the dark.

Sampling Interval (days)	1		7		28		70	100	
Replicate	A	B	A	B	A	B	A	A	B
Transfluthrin (NAK 4455)	60.51	73.23	43.53	15.62	9.68	11.48	2.24	1.86	3.29
NAK 4452	5.59	7.04	25.43	52.86	n.d.	n.d.	n.d.	n.d.	n.d.
NAK 4723	n.d.	0.85	2.31	16.46	79.84	83.35	75.96	72.86	72.97
Remainder	n.d.	4.17	3.92	6.32	1.50	3.90	1.23	1.28	1.49
Water	48.08	25.20	30.76	63.80	56.77	56.64	52.50	53.60	52.70
Total sediment	25.69	68.49	48.61	29.66	39.66	48.48	33.61	30.47	33.06
Extracted residues	--	59.93	42.90	26.96	34.08	41.87	26.53	22.55	25.11
Unextracted residues	--	8.56	5.71	2.70	5.58	6.61	7.08	7.92	7.95
Total volatiles	0.35	0.17	1.55	0.53	1.93	1.50	5.55	13.20	11.78
CO ₂	0.01	0.02	0.03	0.03	1.77	1.27	5.14	13.35	11.84
Volatile organics	0.35	0.16	1.52	0.51	0.27	0.29	0.49	0.33	0.33
Mass balance	--	93.86	80.92	93.98	98.37	106.62	91.66	97.27	97.55

Data obtained from Appendix 14, p. 41, and Appendix 21, p. 48, of the study report.

Concentration in extracted sediment calculated as total sediment minus unextracted residues. Residues in the PU plugs calculated from Appendix 17, p. 44.

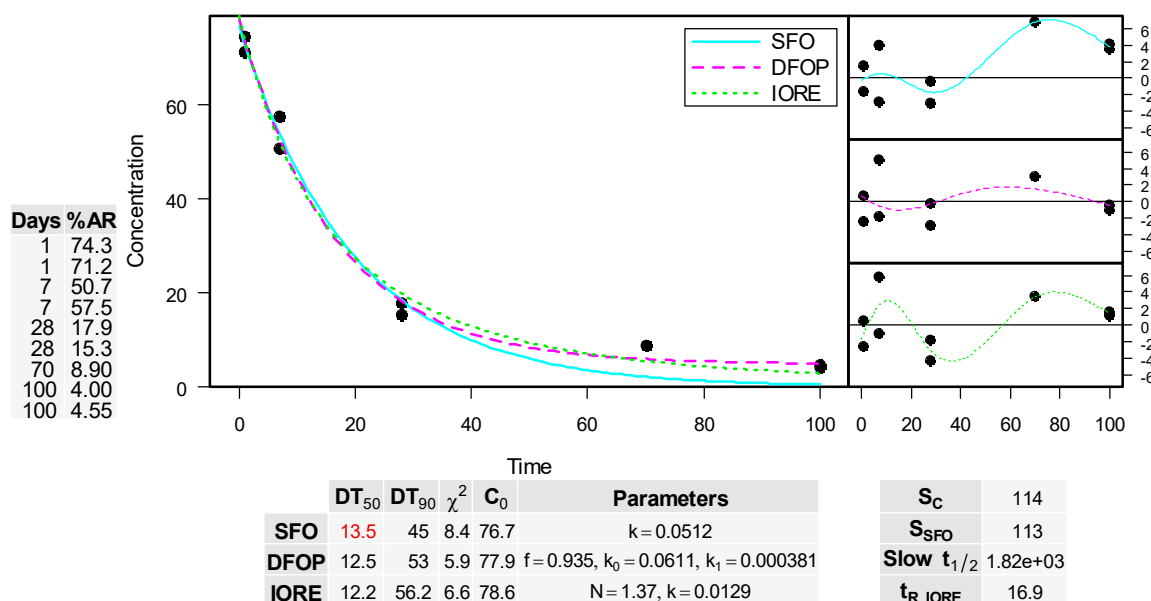
n.d. = not detected.

-- = The sample was lost during sediment extraction.

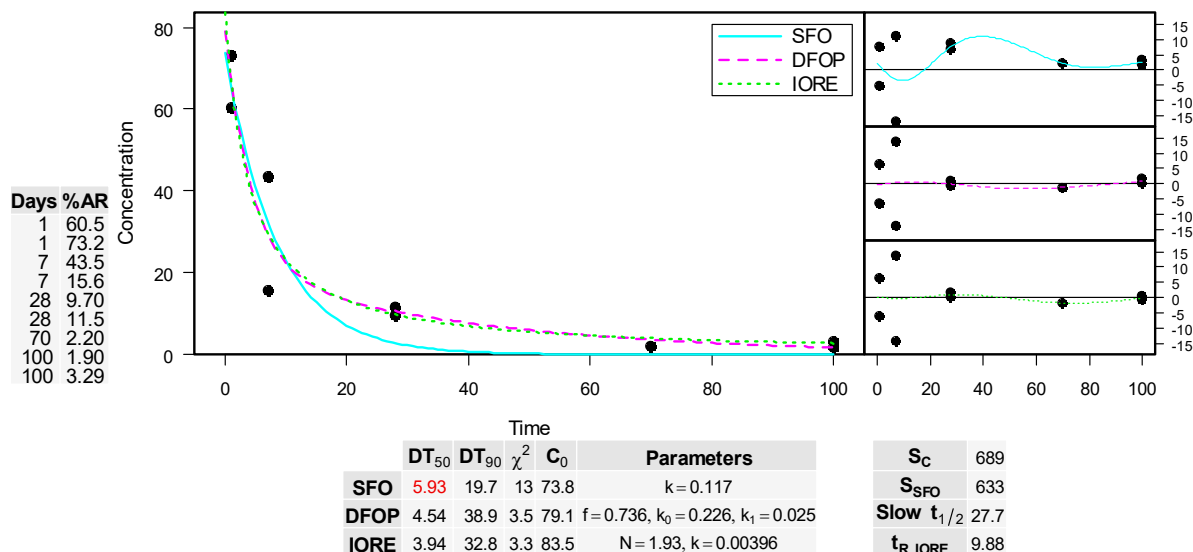
E. Transformation of Parent Compound: Transformation kinetics of the parent compound in the total system are summarized in the following two **Figures**, with transformation product information summarized in **Table 8**.

The study author estimated total system transfluthrin half-lives of *ca.* 8 days in the Laacherhof water:silt loam sediment and <5 days in the Hönniger Weiher water:silt loam sediment (calculations not described; p. 25).

Transfluthrin in Laacherhof aerobic water:silt loam sediment (darkness)



Transfluthrin in Honniger Weiher aerobic water:silt loam sediment (darkness)



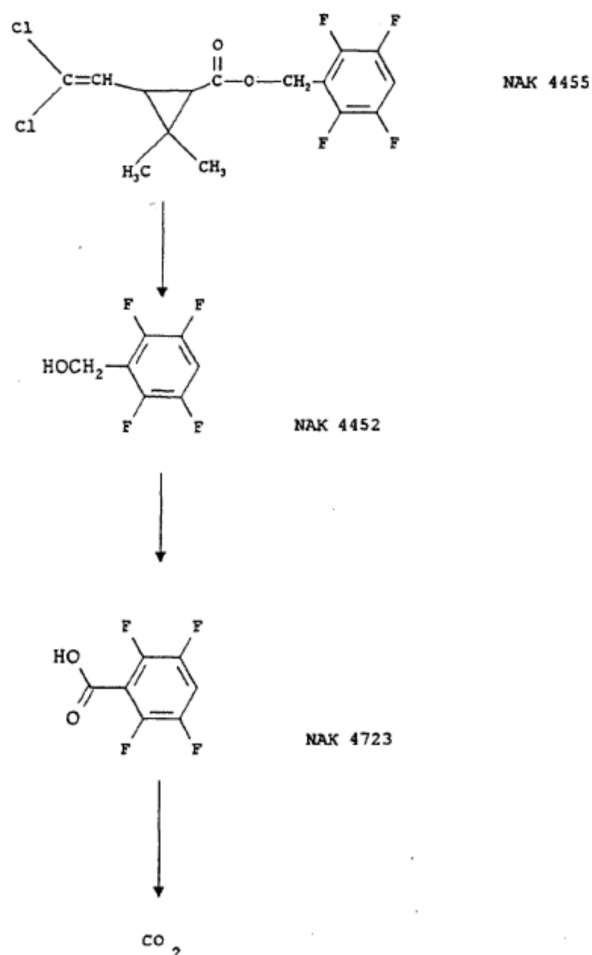
Kinetics models: Single First Order (SFO); Double First Order in Parallel (DFOP), and Indeterminate Order Rate Equation (IORE) in accordance with NAFTA kinetics guidance (USEPA, 2012).

Table 8. Transformation Products of Transfluthrin in Aerobic Water:sediment systems.

	Transformation Products	Maximum %AR Observed	Associated Interval (days)	Final %AR Observed	Final Interval (days)
Germany Laacherhof Water:silt loam sediment (20°C, water pH 8.7, sediment pH 6.5)	NAK 4452	6.43	1	n.d.	100
	NAK 4723	80.63	70	70.47	100
Germany Hönniger Weiher Water:silt loam sediment (20°C, water pH 7.6, sediment pH 5.4)	NAK 4452	52.86	7	n.d.	100
	NAK 4723	83.35	28	72.97	100

Data obtained from Appendix 21, p. 48, in the study report.
n.d. = not detected.

A transformation pathway was not provided by the study author (Appendix 32, p. 59).



III. Study Deficiencies and Reviewer's Comments

1. The first sample was not collected until 1 day posttreatment, at which time transfluthrin was only 73.23-74.30% of the applied (Appendix 21, p. 48). Also, sampling intervals were widely spaced, so that in some cases the concentrations of transformation products changed abruptly between intervals.
2. Material balances were variable in both test systems and <90% of the applied at 100 days in the Laacherhof water:silt loam sediment systems (Appendix 21, p. 48). The study author suggested that the poor material balance may have been a result of the soda lime used to adsorb CO₂ being insufficient for 100 days (p. 20). It was not reported whether the volatile traps were exchanged at each sampling interval.
3. Concentration of transfluthrin and its transformation products in the filtered water and sediment extracts were reported only as KBq and percent of recovered (Appendix 18, p. 45; Appendix 20, p. 47). The reviewer could not precisely generate the total concentration values reported in Appendix 21 (p. 48) by summing values presented in Appendix 18 (water concentrations) and

Appendix 20 (sediment concentrations). Also, concentrations of volatiles in the PU foam (Appendix 17, p. 44) plus the CO₂ concentrations in Appendix 21 (p. 48) do not sum to the total residues in the “trap plug” reported in Appendix 14 (p. 41).

4. Pesticide use history at the sediment source sites was not described, and it was not confirmed that the test systems were pesticide-free prior to use.
5. It was not stated if the samples were stored prior to analysis. Conditions of storage when samples were not in use were not described.
6. Limits of Detection and Quantification were not reported.
7. The study author reported that “the height of the supernatant approx. 6 cm” on p. 14, but shows the water layer was “approx. 4.5 cm above the sediment” in Appendix 1 (p. 28). Since the sediment was “not higher than approx. 2 cm”, these values (6 and 4.5 cm) are comparable only if the water in the sediment is included as part of the “supernatant”.
8. An additional experiment was conducted with Hönniger Weiher water:silt loam sediment where samples were incubated under greenhouse conditions and exposed to light (p. 14). Single samples (entire vessels) were collected at 1, 7, 28, and 100 days posttreatment. Transfluthrin dissipated more rapidly than in the samples kept in darkness (SFO DT50 5.93 days vs 2.35 days). NAK 4452 and NAK 4723 were major transformation products; the patterns of formation and decline were similar to the samples held in darkness (Appendix 21, p. 48).

Transfluthrin in Honniger Weiher aerobic water:silt loam sediment (light)

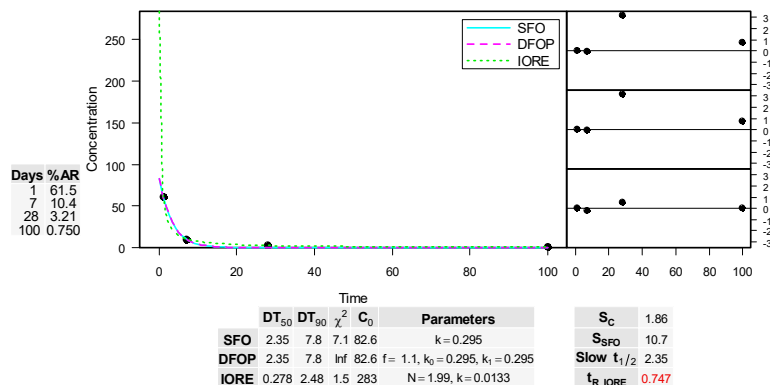


Table 9. Aerobic transformation of Transfluthrin, expressed as a percentage of the applied radioactivity, in Hönniger Weiher water:silt loam sediment maintained in the light.

Sampling Interval (days)	1	7	28	100
Replicate	A	A	A	A
Transfluthrin (NAK 4455)	61.47	10.42	3.21	0.75
NAK 4452	12.00	n.d.	n.d.	n.d.
NAK 4723	2.31	66.24	85.21	65.15
Remainder	9.46	9.96	2.34	0.88
Water	34.94	58.93	60.01	43.66
Total sediment	56.88	32.14	37.29	44.78
Extracted residues	49.88	27.12	30.09	23.00
Unextracted residues	7.00	5.02	7.20	21.78
Total volatiles	0.44	0.64	1.19	7.40
CO ₂	0.03	0.07	0.54	7.27

Volatile organics	0.44	0.60	0.76	0.39
Mass balance	92.27	91.71	98.50	95.84

Data obtained from Appendix 14, p. 41, and Appendix 21, p. 48, of the study report.

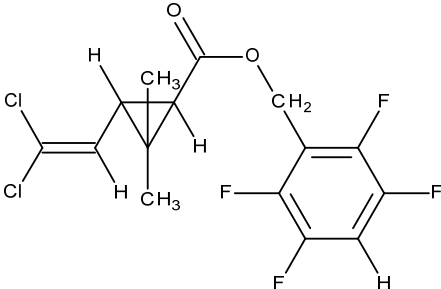
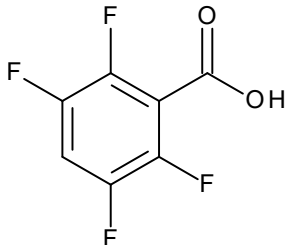
Concentration in extracted sediment calculated as total sediment minus unextracted residues. Residues in the PU plugs calculated from Appendix 17, p. 44.

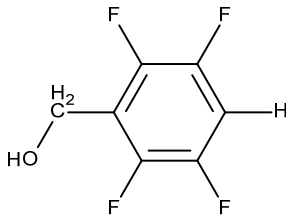

n.d. = not detected.

IV. References

1. U.S. Environmental Protection Agency. 2008. Fate, Transport and Transformation Test - Guidelines, OPPTS 835.4300, Aerobic Aquatic Metabolism. Office of Prevention, Pesticides and Toxic Substances, Washington, DC. EPA 712-C-08-018.
2. U.S. Environmental Protection Agency. 2012. NAFTA Guidance for Evaluating and Calculating Degradation Kinetics in Environmental Media.

DER ATTACHMENT 1. Transfluthrin and Its Environmental Transformation Products.^A

Code Name/ Synonym	Chemical Name	Chemical Structure	Study Type	MRID	Maximum %AR (day)	Final %AR (study length)
PARENT						
Trifluthrin (NAK 4455; Benfluthrin)	<p>IUPAC: 2,3,5,6-Tetrafluorobenzyl (1R,3S)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate</p> <p>CAS: (2,3,5,6-Tetrafluorophenyl)methyl (1R,3S)-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate</p> <p>CAS No.: 118712-89-3</p> <p>Formula: C₁₅H₁₂Cl₂F₄O₂</p> <p>MW: 371.15 g/mol</p> <p>SMILES: Fc1c(F)cc(F)c(F)c1COC(=O)C2C(C)(C)C2C=C(Cl)Cl</p>		835.4300 Aerobic aquatic metabolism	50119705	PRT	PRT
MAJOR (>10%) TRANSFORMATION PRODUCTS						
NAK 4723	<p>IUPAC: 2,3,5,6-Tetrafluorobenzoic acid</p> <p>CAS: Benzoic acid, 2,3,5,6-tetrafluoro-</p> <p>CAS No.: 652-18-6</p> <p>Formula: C₇H₂F₄O₂</p> <p>MW: 194.08 g/mol</p> <p>SMILES: OC(=O)c1c(F)c(F)cc(F)c1F</p>		835.4300 Aerobic aquatic metabolism	50119705	<p>Pond water:Silt loam (oligotrophic)</p> <p>80.63% (70 d)</p>	70.47% (100 d)
					<p>Pond water:Silt loam (Meso/Eutrophic)</p> <p>83.35% (28 d)</p>	72.97% (100 d)

Code Name/ Synonym	Chemical Name	Chemical Structure	Study Type	MRID	Maximum %AR (day)		Final %AR (study length)
NAK 4452	IUPAC: 2,3,5,6-Tetrafluorobenzyl alcohol Formula: C ₇ H ₄ F ₄ O MW: 180 g/mol SMILES: OCc1c(F)c(F)cc(F)c1F		835.4300 Aerobic aquatic metabolism	50119705	Pond water:Silt loam (oligotrophic)	6.43% (1 d)	ND (100 d)
					Pond water:Silt loam (Meso/Eutrophic)	52.86% (7 d)	ND (100 d)
Carbon dioxide	IUPAC: Carbon dioxide Formula: CO ₂ MW: 44 g/mol SMILES: C(=O)=O		835.4300 Aerobic aquatic metabolism	50119705	Pond water:Silt loam (oligotrophic)	3.07% (100 d)	3.07% (100 d)
					Pond water:Silt loam (Meso/Eutrophic)	13.35% (100 d)	13.35% (100 d)
MINOR (<10%) TRANSFORMATION PRODUCTS							
No minor transformation products were identified.							
REFERENCE COMPOUNDS NOT IDENTIFIED							
All compounds used as reference compounds were identified.							

^A AR means “applied radioactivity”. MW means “molecular weight”. PRT means “parent”. ND means “not detected”.

Attachment 2: Statistics Spreadsheets and Graphs

Attachment 3: Calculations

Calculations were performed by the reviewer using PestDF, and the following equations.

Single First-Order (SFO) Model

$$C_t = C_0 e^{-kt} \quad (\text{eq. 1})$$

where,

C_t = concentration at time t (%)

C_0 = initial concentration (%)

e = Euler's number (-)

k = SFO rate constant of decline (d^{-1})

t = time (d)

The SFO equation is solved with R kinetics software by adjusting C_0 and k to minimize the objective function (S_{SFO}) shown in equation 9.

$$DT_{50} = \text{natural log } (2)/k \quad (\text{eq. 2})$$

$$DT_{90} = \ln (10)/k \quad (\text{eq. 3})$$

Indeterminate Order Rate Equation (IORE) Model

$$C_t = \left[C_0^{(1-N)} - (1-N)k_{IORE}t \right]^{\left(\frac{1}{1-N}\right)} \quad (\text{eq. 4})$$

where,

N = order of decline rate (-)

k_{IORE} = IORE rate constant of decline (d^{-1})

This equation is solved with R kinetics software by adjusting C_0 , k_{IORE} , and N to minimize the objective function for IORE (S_{IORE}) (See equation 9). Half-lives for the IORE model are calculated using equation 5, which represents a first-order half-life that passes through the DT_{90} of the IORE model. (Traditional DT_{50} and DT_{90} values for the IORE model can be calculated using equations 6 and 7.)

$$t_{IORE} = \frac{\log(2)}{\log(10)} \frac{C_0^{1-N}(1-0.1^{(1-N)})}{(1-N)k_{IORE}} \quad (\text{eq. 5})$$

$$DT_{50} = \frac{(C_0/2)^{(1-N)} - C_0^{(1-N)}}{k(N-1)} \quad (\text{eq. 6})$$

$$DT_{90} = \frac{(C_0/10)^{(1-N)} - C_0^{(1-N)}}{k(N-1)} \quad (\text{eq. 7})$$

Double First-Order in Parallel (DFOP) Model

$$C_t = C_0 g^{-k_1 t} + C_0 (1 - g)^{-k_2 t} \quad (\text{eq. 8})$$

where,

g = the fraction of C_0 applied to compartment 1 (-)

k_1 = rate constant for compartment 1 (d^{-1})

k_2 = rate constant for compartment 2 (d^{-1})

If $C_0 \times g$ is set equal to a and $C_0(1-g)$ is set equal to c , then the equation can be solved with R kinetics software for a , c , k_1 , and k_2 by minimizing the objective function (S_{DFOP}) as described in equation 9.

DT_{50} and DT_{90} values can be calculated using equations 2 and 3, with k_1 or k_2 in place of k .

Objective Function: SFO, IORE, and DFOP are solved by minimizing the objective function (S_{SFO} , S_{IORE} , or S_{DFOP}).

$$S_{\text{SFO}}, S_{\text{IORE}}, \text{ or } S_{\text{DFOP}} = \sum (C_{\text{model}, t} - C_{d,t})^2 \quad (\text{eq. 9})$$

where,

S_{SFO} , S_{IORE} , or S_{DFOP} = objective function of kinetics model fit ($\%^2$)

n = number of data points (-)

$C_{\text{model}, t}$ = modeled value at time corresponding to $C_{d,t}$ (%)

$C_{d,t}$ = experimental concentration at time t (%)

Critical Value to Determine Whether SFO is an Adequate Kinetics Model

If S_{SFO} is less than S_c , the SFO model is adequate to describe kinetics. If not, the faster of t_{IORE} or the DFOP DT_{50} for compartment 2 should be used.

$$S_c = S_{\text{IORE}} \left(1 + \frac{p}{n-p} F(\alpha, p, n-p) \right) \quad (\text{eq. 10})$$

where,

S_c = the critical value that defines the confidence contours ($\%^2$)

p = number of parameters (3 in this case)

α = the confidence level (0.50 in this case)

$F(\alpha, p, n-p)$ = F distribution with α level of confidence and degrees of freedom p and $n-p$



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5.4300_calculations.xls